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# On the $sp^2$ Configuration and Series Perturbations in the First Spectrum of Indium (In I)

N56-438

Scientific Report #9


~~X66-35931~~ N67-87165
(ACCESSION NUMBER) (THRU)
17 ~~27~~
(PAGES) (CODE)
CR-71011 24
(NASA CR OR TMX OR AD NUMBER) (CATEGORY)
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(NASA-CR-71011) ON THE sp-2 CONFIGURATION AND SERIES PERTURBATICNS IN THE FIRST SPECTRUM OF INDIUM (In I) (Harvard Coll. Observatory) 17 p

N76-70896

Unclas
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NASA CR 71011

On the $sp^2$ Configuration and
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First Spectrum of Indium (In I)

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By

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Pre-Publication Copy

NASA Offices and Research Centers Only

January 1966

(Note: This copy is not necessarily in final form for publication.)

The first spectra of the Group III A elements, Al, Ga, In, Tl, contain interesting features, associated with the terms ($^4P$, $^2D$, $^2P$, $^2S$) of the $sp^2$ configurations and their combinations with the ground-doublet term ($s^2p\ ^2P^o_{\frac{1}{2},\frac{3}{2}}$).

In each of the spectra Al I, Ga I, In I the quartet term is well established, is almost "pure" in the LS-designation, and lies deep (Moore 1949, 1952, 1958). In Tl I, though the term is still well represented by the LS symbol, it lies much higher in relation to the terms of the series spectrum and the spin-orbit splitting is large, so that the $^4P_{\frac{1}{2}}$ lies below the series limit and perturbs the $^2S$-series, whereas $^4P_{\frac{3}{2}}$ lies about 540 $cm^{-1}$ above the ground 6 $^1S_o$ term of the ion and autoionizes strongly into the $s^2E$ (d) $^2D_{\frac{3}{2}}$ continuum; the $^4P_{\frac{5}{2}}$ level is less definitely placed about 3790 $cm^{-1}$ above the 6 $^1S_o$ limit.

The positions of the $sp^2$ $^2D$ terms in these spectra have constituted a long-standing problem. The earlier idea that the term lies deep in each of the spectra Al I, Ga I and In I, and is effectively absorbed into $^2D$-series as the first or second member, was suggested by the observation that these spectra contain anomalies in fine structure splittings, the second $^2D$ series members having larger splittings than the first and third members. This placing of $sp^2$ $^2D$ and the interpretation of the splitting anomaly certainly now seem correct in the case of Al I, but not in Ga I and In I, where the doublet splitting anomalies are more probably due to perturbations by the $sp^2$ $^4P$ terms, a suggestion made by Professor B. Edlén in private communication to one of us (W.R.S.G.).

In 1961, Garton and Codling suggested, from a study of the relative behaviour of the quantum defects in the In I $s^2ns\ ^2S$ and $s^2nd\ ^2D$ series, that in this spectrum the $sp^2\ ^2D$ term lies buried in the $s^2E\ (d)\ ^2D$ continuum, so that the photoionization cross-section possesses a broad maximum centered about 2700 $cm^{-1}$ above the first ionization potential. An additional peculiarity reported in the same paper, but not at that time explicable, was an intensity minimum in the $5s^25p\ ^2P^o_{\frac{1}{2},\frac{3}{2}} - 5s^2nd\ ^2D_{\frac{3}{2},\frac{5}{2}}$ absorption series near n = 9. The illuminating theoretical treatment given by Fano in 1961, concerning line shapes and intensity distributions to be expected when "resonances" between discrete terms and/or continua are present, provides a likely explanation of this intensity peculiarity. A similar situation,of the "Beutler-Fano" resonance maximum lying in the continuum but the minimum of the profile lying in the converging line series, is found in Ba I, but the separation in In I is much larger, if the suggested interpretation is correct. A recent paper by Penkin and Shabanova (1965) questions the conclusions of Garton and Codling (1961) concerning the perturbation of the $^2D$-series of In I, so that it seems appropriate to review the evidence used in the arguments presented in the 1961 paper, before presenting evidence from more recent work which supports these previous conclusions.

The first argument that $sp^2\ ^2D$ in In I lies in the continuum is based on the curves showing $n^*-n$ versus $T_n$ for the S- and D-series, shown in Fig. 1 of the paper by Garton and Codling (1961); the curves were derived from measurements to an estimated accuracy of 0.004Å on absorption line series recorded to about n = 30. Penkin and Shabanova (1965) have reported new measurements on the same series, at rather lower dispersion and with an estimated accuracy of 0.03Å. These workers remark that Garton and Codling, because of an unsuitable choice of the value of the limit, were led to a false conclusion that the $^2D$-series terms of In I suffered perturbations from the presence of $sp^2$ $^2D$ beyond that limit. We have considered the contention of Penkin and Shabanova and find it cannot be sustained. There is no question that the $s^2nd$ $^2D$ quantum-defect plot shows a marked downward curvature in the direction of increasing n, when the whole series is plotted; this is illustrated in Fig. 1 here shown, from which it is clear that no adjustment of the limit value can produce a straight line plot. The fact that the n*-n versus $T_n$ graphs of Penkin and Shabanova (1965) appear straight is partly due to the cramped scale employed in the reproduction, and partly to omission of terms from n = 5 to 8, inclusive of the $^2D$-series. Penkin and Shabanova also remark that the $^2S$- and $^2D$-series measurements of Garton and Codling (1961) can be made to give straight-line quantum defect plots by a change of limit of $-0.43\ cm^{-1}$. That this is not so is demonstrated in Fig. 2, in the case of the $^2S$-series; the fractional change of limit mentioned has a negligible effect on the $^2D$-curve in Fig. 1, except at the points representing the last few members of the series.

Moreover, consideration of the magnitude of the error (0.03Å) stated by Penkin and Shabanova to affect the measurements, casts doubt upon the validity of their effort to adjust the limit in their fashion, viz., to $0.1\ cm^{-1}$. The error in (n*-n) for an error T in absolute term values, owing to limited wavelength accuracy, increases rapidly for high terms, as can be seen from $\Delta n^* = -\frac{1}{2}\frac{R^{\frac{1}{2}}}{T^{\frac{3}{2}}}\Delta T$. At the top of Fig. 2, we have drawn the range of the error $\Delta n^*$, due to an error $\Delta T = 0.13\ cm^{-1}$, corresponding to $\Delta\lambda = 0.006$Å at 2150Å. It is immediately apparent that, even with an accuracy of wavelength measurement of this order, there is little point in attempting to manipulate the limit to an accuracy of 0.1 $cm^{-1}$; the ordinate of the upper part of Fig. 2 will, of course, be multiplied by a factor of 5 if the wavelength measurements are limited to 0.03Å. It seems, therefore, that on the basis of the measurements to date, the limit is probably known to 0.3 $cm^{-1}$ or a little better, but not to 0.1 $cm^{-1}$. We have thought the measurements reported by Garton and Codling (loc. cit.) reliable, partly because of the good agreement of the $s^2ns\ ^2S_{\frac{1}{2}}$ values derived from the combinations with $5\ ^2P_{\frac{1}{2},\frac{3}{2}}$ respectively. However, systematic errors may affect the data, and an experiment is being undertaken currently by Dr. F.S. Tomkins of the Argonne National Laboratories, who is in a position to photograph much longer absorption series with the very high dispersion of the second or third order of a 30-ft. grating instrument. One typographical error in the tables of Garton and Codling should be mentioned at this point. In table III of the paper cited, the line $5s^25p\ ^2P^o_{\frac{1}{2}} - 5s^2nd\ ^2D_{\frac{3}{2}}$ for n = 14 should be given as 2180.549Å.

Returning to the perturbed course of the $s^2nd\ ^2D_{\frac{3}{2},\frac{5}{2}}$-series, we have fitted the measurements (Garton and Codling loc. cit.) to the type of formula for the effective quantum number used by Shenstone and Russell (1932). Writing this as

$$n^*-n = a + b\,T_n + \frac{\alpha}{T_n - T_\circ}$$

with $T_\circ = -2700\ cm^{-1}$ and the constants $a = -2.06602$, $b = -7.314 \times 10^{-6}$ and $\alpha = -1.028 \times 10^3$, derived from a least-squares reduction of the term values given in Table III of Garton and Codling (1961), we find the following residuals (calculated minus observed term values):

n = 7-31, +5, -2.5, -2.5, -1.9, -0.5, +0.4, +0.4, +0.7, +0.7, +0.6, +0.6, +0.35, +0.3, +0.25, +0.1, +0.1, +0.0, -0.1, -0.5, - 0.05, -0.1, -0.05, -0.05, -0.15, -0.15 $cm^{-1}$

Seemingly, the supposition that $5s5p^2\ ^2D$ lies roughly 2700 $cm^{-1}$ above the first ionization limit is observationally well founded. As already mentioned, much more precise measurements of the wavelengths of the series lines will be shortly undertaken at Argonne, so that it is not worthwhile for us to repeat measurements at the dispersion previously used. Some recent indications from theory on the position of the perturbing $^2D$ term in In I are mentioned below. In the case of the Ga I spectrum, some unpublished measurements on long series, made several years ago at Imperial College by E.M. Reeves and A. Bass, have suggested a downward curvature of the quantum defect plot of the $^2D$-series similar to, but less marked than, that shown in Fig. 2. However, since again the measurements will shortly be repeated at Argonne, the Imperial College measurements are now regarded as obsolete. A significant point is that, as in In I, an intensity anomaly exists in Ga I in the $^2D$-series around n = 9.

We next consider the nature and location of the terms $sp^2\ ^2S$, $^2P$. These terms are certainly and clearly distinguished as nearly pure LS-states, located above the first ionization potential, in Al I, the $^2S$ term combining with the ground doublet term to give a pair of strongly autoionizing lines near 1930Å (Garton, 1950; Garton, Parkinson and Reeves, 1965) and the $^2P$ combining with the ground-term, to form the "P-P'" group of four lines around 1765Å. In Ga I (Garton, 1952) a similar group of 6 strong absorption lines has been given a corresponding interpretation, but in In I (Garton 1954) the absorption spectra previously reported have contained a group of only 5 -- instead of 6 -- lines. An admittedly rather tentative argument, based on jj-coupling intensity rules was used to suggest that the missing member was $5\ ^2P_{\frac{1}{2}} - 5s5p^2\ ^2S_{\frac{1}{2}}$. A good picture of the portion of the In I spectrum concerned is to be found elsewhere (Garton 1962). Effectively, $5\ ^2P_{\frac{3}{2}} - 5s5p^2\ ^2S_{\frac{1}{2}}$ designation was assigned to the strongly autoionized line at 1757Å, the other four lines forming the "P-P'" multiplet. This interpretation of the In I absorption line group has been proved certainly in error by the recent work on f-values reported by Heppinstall (1965), who points out that the above specification of the line at 1757Å would require the improbably high f-value of 1.26, and replaces the earlier identification by $5\ ^2P_{\frac{1}{2}} - 5s5p^2\ ^2S_{\frac{1}{2}}$.

Heppinstall's (loc. cit.) work indicated at once that the "missing" line of the group should lie at 1828.3Å. A re-examination of a number of furnace-absorption spectra acquired at Imperial College failed to show any suggestion of a line in this neighbourhood. On the supposition that the missing absorption line might be brought out by increasing sufficiently the $5\ ^2P^{\circ}_{\frac{3}{2}}$ level population, new absorption spectra of indium vapour at temperatures in the range 5000 - 6000° have been obtained with the Harvard shocktube apparatus previously described (Garton, Parkinson and Reeves, loc. cit.). The spectra obtained show clearly a weak diffuse absorption feature at the correct position, viz. 1828.3Å. A comparison of the two spectra reproduced in the plate, with the furnace spectra of an earlier reference (Garton 1962), illustrates that, with increasing vapour density, and with the $5\ ^2P_{\frac{3}{2}}$ level sufficiently populated, the 1828.3Å line becomes just observable before the general continuous absorption underlying it drowns out all structure.

Theoretical explanation of the extreme weakness of the 5 $^2P_{\frac{3}{2}}$ - $5s5p^2$ $^2S_{\frac{1}{2}}$ component is likely to be rather complex.

Dr. J.M. Wilson of Imperial College is currently engaged in theoretical studies of the four isoelectronic sequences beginning with Al I to Tl I, and allows us to quote from his results. In the first place, Slater-type calculations on the $sp^2$ configuration, with the parameters initially established without assumption of the locality of the $sp^2$ $^2D$ term, predict that this will lie in the neighbourhood suggested by Garton and Codling (1961), i.e., roughly 2700 $cm^{-1}$ above the 5 $^1S_o$ limit. Furthermore, Wilson has diagonalized the whole energy matrix and performed a least-squares adjustment of the Slater parameters, finding thereby an r.m.s. deviation of the calculated minus observed levels of 95 $cm^{-1}$, i.e., to within 0.4% of the total width of the configuration. A calculation of the degree of mixing of the three $j = \frac{1}{2}$ levels (in LS-notation $^4P$, $^2P$, $^2S$) shows that the level previously listed as $^2P_{\frac{1}{2}}$ at 59657 $cm^{-1}$ (Garton 1954) is to be regarded as constituted of 64% $^2P_{\frac{1}{2}}$ and 36% $^2S_{\frac{1}{2}}$, and the level previously marked $^2S_{\frac{1}{2}}$ at 59118 $cm^{-1}$, - now corrected to 56906 $cm^{-1}$, - correspondingly may be labeled 36% $^2P_{\frac{1}{2}}$ plus 64% $^2S_{\frac{1}{2}}$. Full details of the theoretical work on the isoelectronic sequences mentioned will be published by Dr. Wilson shortly. It is worth remark that some assignments of absorption lines of In I, other than the 1757Å line discussed above, given in Table I of the Garton (1954) reference will then need reconsideration. Thus, three lines between 1172 and 1320Å, previously classified as members of the series 5 $^2P^o_{\frac{3}{2}}$- 5s5p np $^2S_{\frac{1}{2}}$ converging on In II 5s5p $^3P^o_2$ need reassignment. In fact, it seems certain that the upper states of the lines cannot be labeled with LS-symbols, and it is more probable that they converge on

5s5p $^3P_1^o$ of In II.

## ACKNOWLEDGEMENTS

We are indebted to Mr. R. Heppinstall of Reading University for sight of his oscillator strength determinations ahead of publication, and to Dr. J.M. Wilson of Imperial College for permission to quote some results from his theoretical studies. We also wish to thank Mr. W. Bingham for his technical assistance in performing the shock tube experiments.

This work has been supported by NASA Grant NsG-438 and Contract NONr-1866(48) of the Office of Naval Research.

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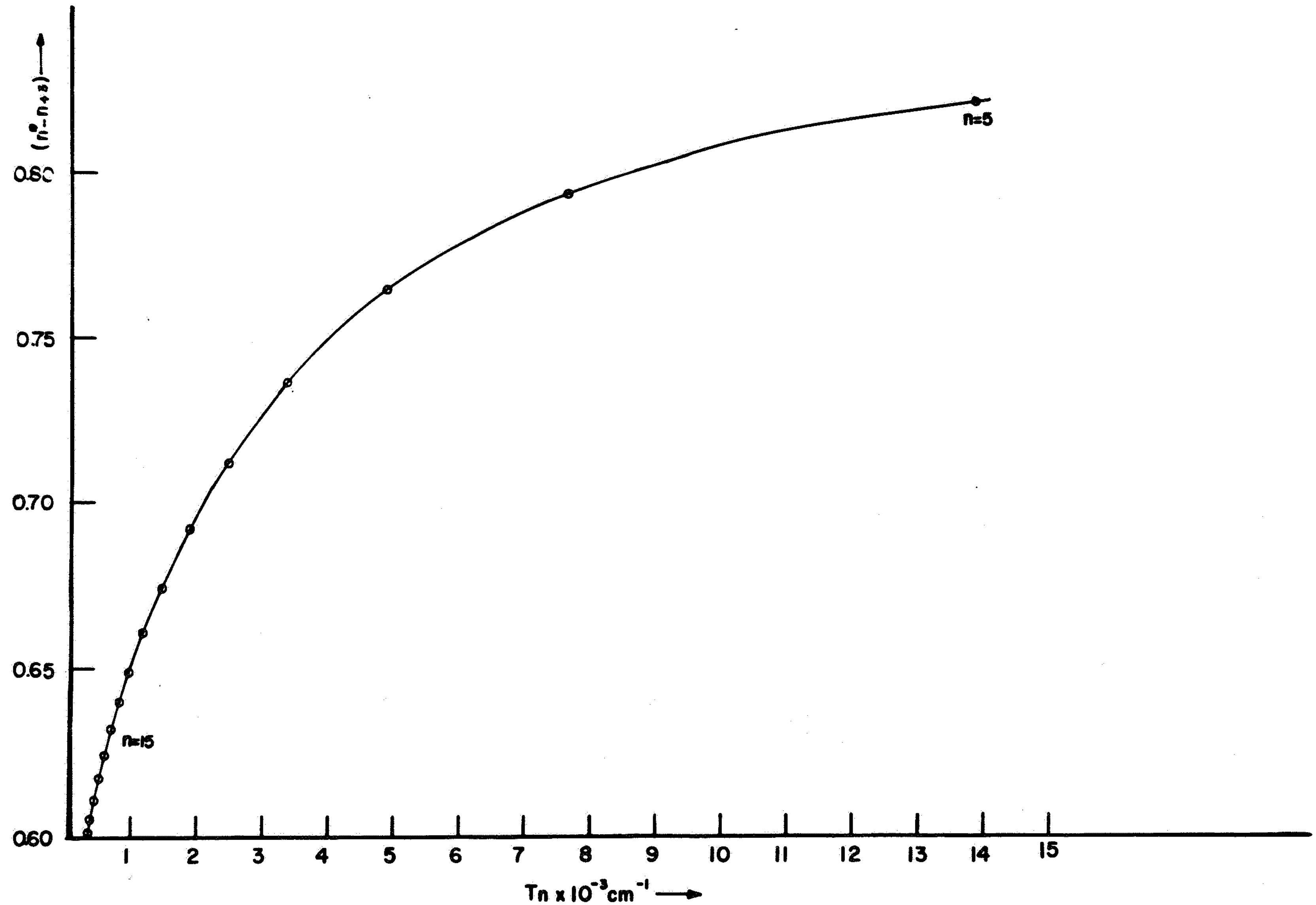



Fig. 1 Plot of quantum-defect for the $s^2nd\ ^2D_{\frac{3}{2}}$ levels of In I; limit 46669.9 cm$^{-1}$.

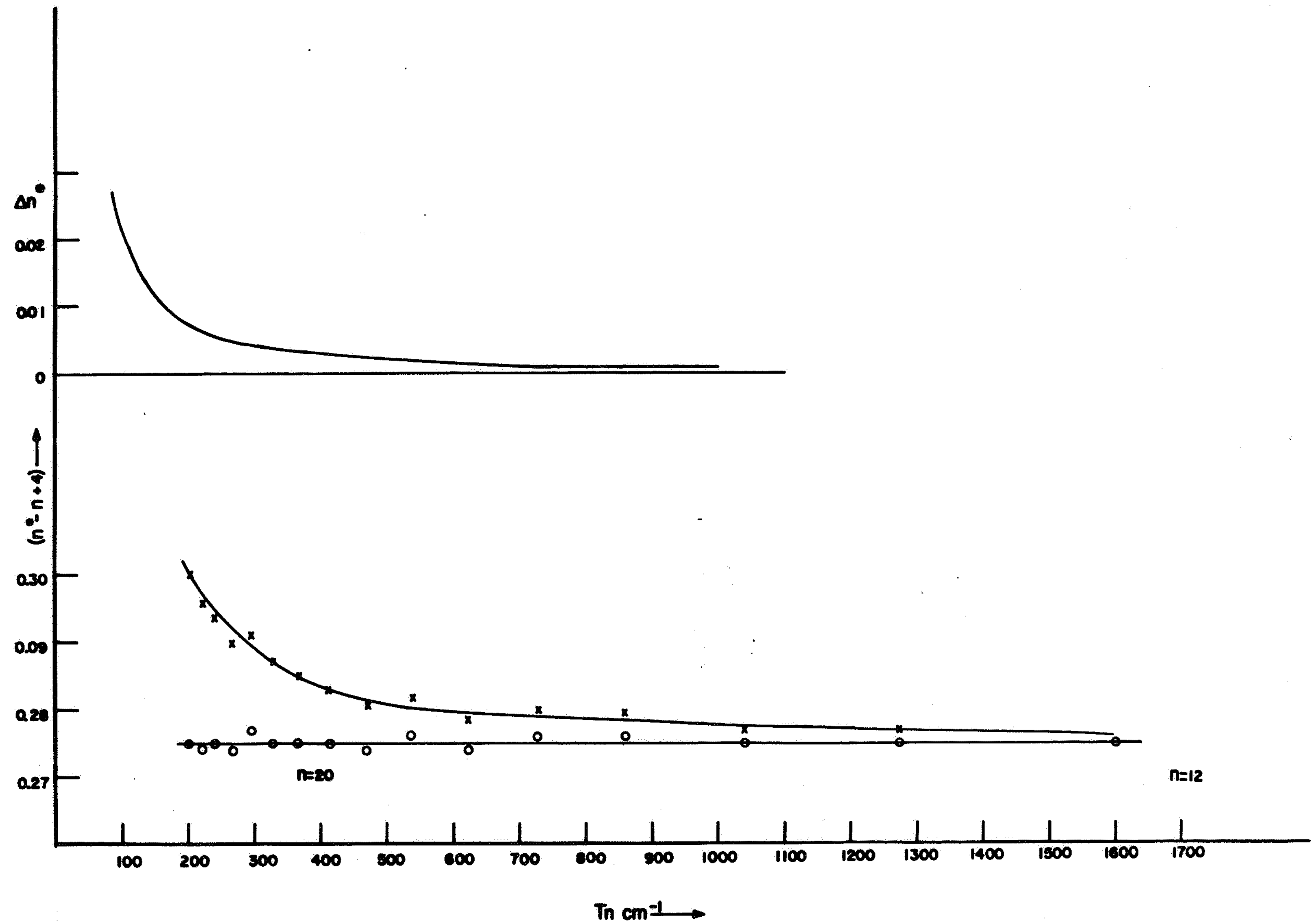


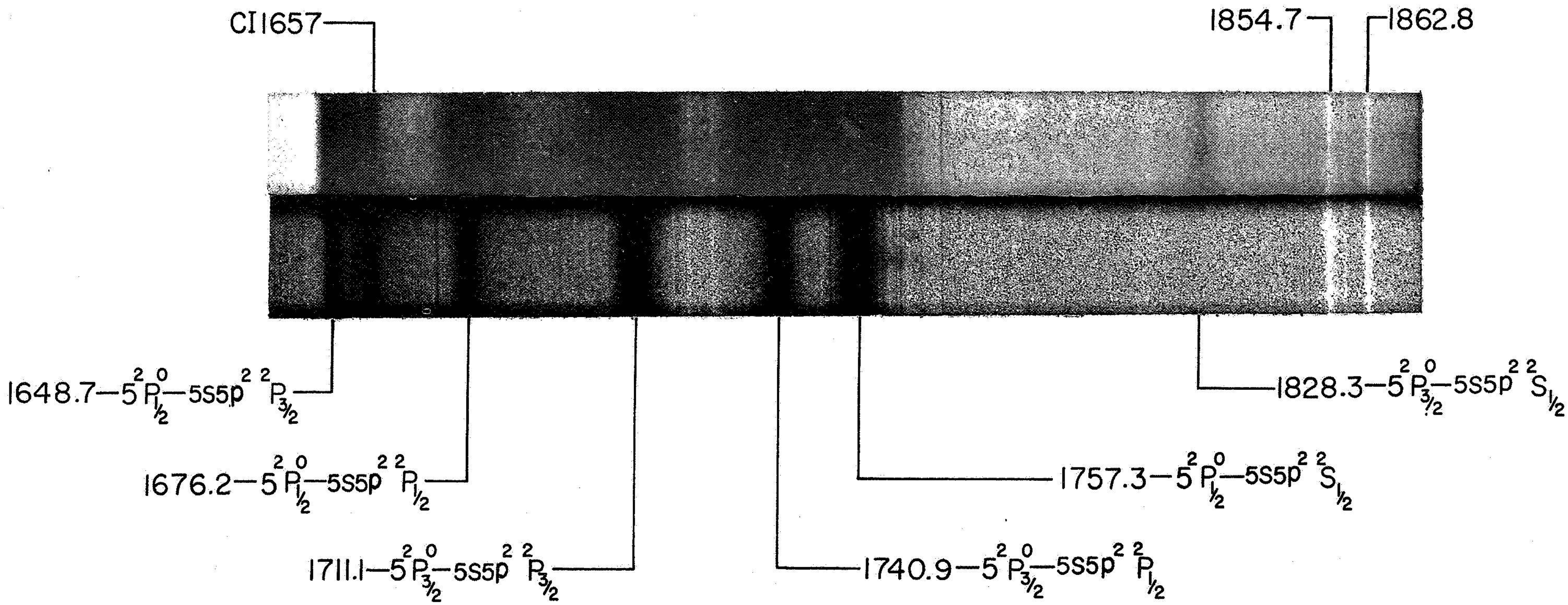

Fig. 2 Below: Plot of quantum-defect for the $s^2ns\ ^2S_{\frac{1}{2}}$ levels of In I, ○ - limit 46669.93 $cm^{-1}$, x - limit 46669.5 $cm^{-1}$.

Above: Error in ($n^*-n$) corresponding to

$$\Delta\upsilon = \frac{\Delta\lambda}{\lambda^2} = \frac{0.006\ \text{Å}}{\lambda^2}$$

or similar error in location of limit.

# ABSORPTION SPECTRUM OF SHOCK-HEATED INDIUM



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| 1. ORIGINATING ACTIVITY (Corporate author) Harvard University | 2a. REPORT SECURITY CLASSIFICATION | |
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| 3. REPORT TITLE On the $sp^2$ Configuration and Series Perturbations in the First Spectrum of Indium (In I). | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) | | |
| 5. AUTHOR(S) (Last name, first name, initial) W.R.S. Garton, W.H. Parkinson and E.M. Reeves | | |
| 6. REPORT DATE January 1966 | 7a. TOTAL NO. OF PAGES 13 | 7b. NO. OF REFS 11 |
| 8a. CONTRACT OR GRANT NO. NASA NsG-438 ONR NONr-1866(48) | 9a. ORIGINATOR'S REPORT NUMBER(S) #9 | |
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13. ABSTRACT


The absorption spectrum of shock-heated indium vapour has been photographed, and the missing member of the six-line group ($^2P_{\frac{1}{2},\frac{3}{2}}$ - $sp^2$ $^2S$, $^2P$) identified at 1824 Å.

The $sp^2$ configuration and the series perturbation in In I has been reviewed and the term $sp^2$ $^2D$ confirmed as the perturber of the $^2D$-series.


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